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LANTHANUM MONOXIDE

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Lanthanum Monoxide

It was reported in Technical Report VII (p.96) that a sample of lanthanum metal filings which had been annealed at 475° for 52 hours gave a powder diffraction pattern corresponding to two f.c.c. lattices, with cell constants of 5.307 ± 0.005A. and 5.249 ± 0.005A. The data are given in Table 20 at the end of this report. The first number corresponds to the lattice constant of f.c.c. lanthanum, which was reported as 5.296 ± 0.005A. by Ziegler et al. (1953).

An attempt was made to identify the second f.c.c. phase, having a_o equal to 5.249 Å. It seemed most likely that this would be either an oxide or a nitride phase. No hitherto reported lanthanum oxide has a f.c.c. structure,[1] but Ellinger & Zachariasen (1953) have reported a f.c.c. samarium monoxide, SmO, with the NaCl-type structure, and a slightly variable lattice constant. The Sm-Sm distance in this monoxide is approximately 0.04 Å. smaller than in the metal. The authors have identified this phase with the grey coating formed on metal pieces on heat treatment.

Lanthanum nitride, LaN, has been described by Young & Liegler (1952) as having the NaCl-type structure, with a_o equal to 5.295 ± 0.004 Å. (5.284 ± 0.004 kX.)[2] on the basis of calculations of intensity ratios for adjacent lines for this and other structures considered as possible. A comparison of measured intensity ratios from the two sets of lines found in this investigation with the intensity ratios calculated by Young & Liegler for f.c.c. lanthanum and for LaN indicates that the lattice to which the cell constant of 5.249 Å. corresponds does have the NaCl-type structure.

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[1] The strong lines of the b.c.c. modification of La_2O_3 form an apparent f.c.c. lattice, but with a much larger a_o, namely 5.7 Å. This is discussed further below.

[2] Landelli & Botti (1937) had previously reported 5.286 Å. (5.275 kλ.).

This comparison is made in Appendix III, Table 21. The principal evidence lies in the relative weakness of the lines with Σh_i^2 equal to 11 and 19. Since this lattice constant is so different from that of the nitride, it is concluded that it corresponds to that of a monoxide, LaO, similar to SmO. It may be noted that the La-La distance in the presumed monoxide is also about 0.04 A. less than in the metal.

Ziegler, Young & Lloyd (1953), in an investigation of the crystal structure of lanthanum metal, reported that the principal f.c.c. pattern, ascribed to f.c.c. (β-) lanthanum, was usually accompanied by some lines from h.c.p. (α-) lanthanum, as well as by a number of weak lines which were assignable to two different f.c.c. lattices, one having a lattice constant 0.5-1% less than that of f.c.c. lanthanum, and the other having a_o between 5.63 and 5.66 A. The former of these, called the "y" structure by the authors, and for which no explanation was suggested, corresponds to the lanthanum monoxide lattice described above.

The second extra f.c.c. lattice appearing was ascribed by the authors to lanthanum hydride. However, it seems unlikely that there should have been any hydride present in the metal sample. If there had been some originally present, the hydrogen should have been effectively

removed by the 13 hours' heating at 700° C. under high vacuum to which one sample was subjected, but for which the "hydride" structure persisted. It is suggested here that the lines of the "hydride" pattern are actually the stronger lines of the b.c.c. form of La_2O_3 (often called the C-modification) (Löhberg, 1935; Bommer, 1939), which appear to belong to a f.c.c. lattice half as large, because the metal atoms lie in a slightly distorted face-centered cubic array (Strukturbericht II, 38-40). If this were so, the b.c.c. lattice to which the lines of the "hydride" structure would correspond would have a cell constant of twice 5.66 A., or 11.32 A., to make it as large as possible. The actual b.c.c. parameter has not been very accurately determined, being reported as 11.4 kX. units by Lohberg on the basis of only four blurred measured lines, with considerable deviation. This appears to be a reasonable explanation, if not a conclusive one, of what Ziegler, Young & Floyd considered to be an appearance of the hydride.

TABLE 20.--X-ray diffraction data for lanthanum metal sample, annealed. Cu radiation, Ni filter. See p. 96

	f.c.c. La			LaO		
sin θ obs.	$\sum h_i^2$	a_o	I_{obs}	$\sum h_i^2$	a_o	I_{obs}
0.2547	3	5.243		3	5.243	
.2932	4	5.258				
.2955				4	5.217	
.4129	8	5.281	40			
.4176				8	5.221	40
.4836	11	5.286	70			
.4892				11	5.226	50
.5050	12	5.289	20			
.5102				12	5.234	20
.5822	16	5.296	10			
.5890				16	5.236	10
.6345	19	5.296	40			
.6414				19	5.239	35
.6712	20	5.294	40			
.6578				20	5.241	40
.7120	24	5.304	30			
.7203				24	5.243	35
.7551	27	5.305*	40			
.7634				27	5.248*	40
.8222	32	5.304*	10			
.8311				32	5.247*	15
.8589	$35\alpha_1$	5.306*	70			
.8684				$35\alpha_1$	5.248*	
.8705	$36\alpha_1$	5.309*	40			
.8807				$36\alpha_1$	5.248*	50
.9178	$40\alpha_1$	5.308*				
.9276				$40\alpha_1$	5.252*	60
.9620	$43\alpha_1$	5.305*				
.9623	$44\alpha_1$	5.310*		$43\alpha_1$	5.249*	
.9727				$44\alpha_1$	5.253*	

Average a_o values computed using starred values are 5.307 ± 0.005 A. (f.c.c. La) and 5.249 ± 0.005 A. (LaO).

See Technical Report I for references